

Shock-Induced Transformation of Al_2O_3 and LiF into Semiconducting Liquids

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(Received 2 August 2002; published 18 July 2003)

Shock compression of sapphire (Al_2O_3) and lithium fluoride (LiF) to pressures above 5 Mbar has been observed to transform these transparent, wide band-gap insulators into partially degenerate liquid semiconductors with optical reflectivities of several percent. Reflectivities rise steadily with shock pressure up to 45% in sapphire at 20 Mbar and 20% in LiF at 13 Mbar. Using a simple model, the electron scattering length was inferred to be approximately the interatomic distance. In addition, several equation-of-state points at these pressures were measured.

DOI: 10.1103/PhysRevLett.91.035502

PACS numbers: 62.50.+p, 64.30.+t, 64.70.-p, 71.22.+i

All insulators are expected to transform into metals at high enough compression due to closing of the energy gap in the density of states separating occupied and unoccupied states [1]. Such pressure-induced gap closure will be preceded by a stage when thermal excitation can excite substantial numbers of electrons across the reduced gap into unoccupied states. This is particularly relevant to strong shock experiments where compression ratios of a few are accompanied by temperatures of the order of an eV—comparable to the band gaps of insulator materials. For example, previous experiments on deuterium showed that shock conductivity [2] increased gradually with temperature, consistent with semiconducting-type behavior, before reaching saturation where gap closure was inferred. Reflectivity measurements showed that at saturation the conduction electron density was characteristic of a metal [3]. Both these studies required the *a priori* assumption that the electron scattering length was equal to the interatomic distance (the Ioffe-Regel limit). In this paper we examine the effect of shock compression on sapphire (Al_2O_3) and lithium fluoride (LiF), two wide band-gap, transparent dielectrics used extensively in high-pressure studies. We develop a simple, quantitative model to show how the observed onset and gradual rise of optical reflectivity is driven by thermal activation of electrons across a reduced energy gap in the shocked liquid. The model establishes that the electron conductivity is pinned near the Ioffe-Regel limit throughout the reflectivity rise and illustrates how, for an electron conductivity-type measurement, the semiconductor-metal transition at high temperatures can be a smooth, continuous process.

Sapphire, or corundum, is a covalently bonded crystal with a band gap of ~ 9 eV. In diamond anvil cell (DAC) experiments it is used in the form of ruby as a pressure calibration standard [4], while in shock studies it is important as a high-impedance, transparent window [5,6]. The melting point of sapphire has been measured up to 0.25 Mbar in a DAC [7] and is in agreement with molecular dynamics (MD) simulations [8]. The equation of state (EOS) of sapphire has been measured in shock wave experiments up to 3.4 Mbar [9] where the material

was thought to still be solid but to have undergone a polymorphic phase transition; later shock experiments showed evidence of a phase transition at 0.79 Mbar [10] that was consistent with the transition from the corundum $\alpha\text{-Al}_2\text{O}_3$ structure to the Rh_2O_3 (II) structure observed in earlier DAC studies [11]. Lithium fluoride is an ionic crystal with a band gap of ~ 14 eV that has been used extensively in shock experiments as a window because of its ability to remain transparent up to > 1.6 Mbar [12]. A large discrepancy exists between the Hugoniot melting point of LiF measured in shock experiments (2.8 Mbar) [13] versus that determined in heated DAC's (1.3 Mbar) [14]. The EOS of LiF has been studied up to 4.9 Mbar under shock compression [15]. With the use of laser-induced shock wave techniques it is now possible to substantially extend the range of pressures and temperatures over which both these materials have been examined thus far. In the experiments reported below, the optical reflectivity of sapphire and LiF above 5 Mbar has been measured and several equation of state points between 10 and 20 Mbar have been established.

This experiment was performed on the OMEGA laser at the University of Rochester [16] using two laser pulse types: a shorter 1 ns pulse to impulsively load the specimen and generate a decaying shock wave for reflectivity measurements over a wide pressure range and a longer 3.7 ns pulse to produce a steady shock wave for impedance-matching EOS studies. In the 1 ns pulse, 940 J was delivered in two beams; in the 3.7 ns pulse, 1.7–2.1 kJ was delivered in eight beams. The laser focal region was smoothed using distributed phase plates, producing a uniformly irradiated spot 800 μm in diameter. Targets consisted of the test material (sapphire $\rho_0 = 3.97$ g/cm³ and LiF $\rho_0 = 2.64$ g/cm³), a stepped-aluminum pusher, and a plastic ablator (see Fig. 1 inset for dimensions). The sapphire was oriented in the z -axis direction (c cut) and the LiF in the (100) direction. The aluminum pusher was diamond turned to an rms surface roughness of less than 30 nm over 200 μm . Step heights were measured to an accuracy of 0.2 μm . The front side of the aluminum was coated with 20 μm of plasma polymer as an ablator to the reduce x-ray generation at the laser-plasma interface.

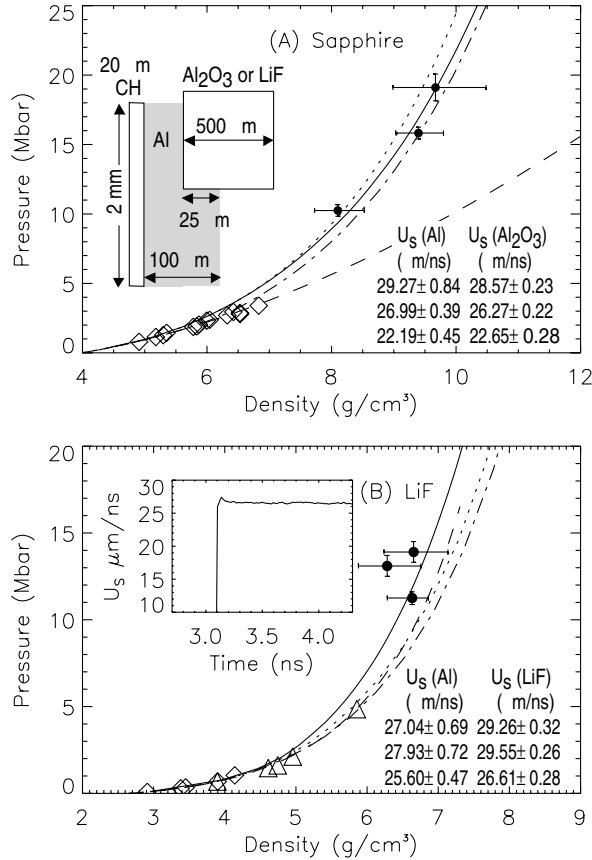


FIG. 1. Hugoniot data and predictions for (a) sapphire and (b) LiF. Data from this study (solid circles) are shown along with predictions from SESAME [20] (solid lines), qEOS [21] (dotted lines), and the modified qEOS [22] (dashed-dotted lines). In (a) the fit to the data from Erskine [9] (diamonds), given by $U_s = 8.74 + 0.96U_p$, is shown as a dashed line. In (b) a best linear fit to the data from Al'tshuler *et al.* (diamonds) and Kormer *et al.* [15] (triangles), given by $U_s = 5.18 + 1.31U_p$, is shown by the dashed line. Insets show the target dimensions and sample shock velocity profiles for the steady shock wave (where time is measured from the start of the laser pulse), along with the raw shock velocity data used to determine the EOS points.

The shock diagnostic used was a line-imaging velocity interferometer system for any reflector (VISAR) [17,18] with a 400 μm field of view. Two VISAR instruments with different velocity sensitivities [19] were used to resolve 2π phase shift ambiguities at shock breakout. The probe source was an injection-seeded, Q -switched yttrium aluminum garnet laser, operating at a wavelength of 532 nm with a stretched pulse length of ~ 25 ns. Streak cameras were used to detect the reflected probe signal allowing time resolutions down to 10–15 ps. The streak camera dynamic range limited the lowest detectable target reflectivity to a few percent since the camera also needed to measure the 85% reflectivity of the aluminum.

Dielectrics shocked to Mbar pressures have been found to strongly absorb optical wavelengths [13], a process we have observed in sapphire and LiF. A further increase in

pressure eventually generates a reflecting shock front and it is in this regime that we focus our experiments; because the shock front is reflecting, the Doppler shift measured by the VISAR is directly related to the shock wave velocity. Three observables are extracted from the VISAR data for each shot: the shock velocity in the initially transparent dielectric versus time, as given by the fringe shifts; the shock reflectivity versus time, as given by the fringe amplitudes; and the average shock velocity in the aluminum pusher, as given by the breakout times from the top and bottom step. To determine EOS points we use the impedance-matching technique with the SESAME [20] aluminum EOS as the reference standard. Typical uncertainties for the average shock speed in aluminum were 1.5%–3% and dominate the errors in inferred pressure and density. Uncertainties in the shock velocity determined from fringe shifts are typically $\sim 1\%$. The data are shown on pressure-density plots in Fig. 1. Absolute reflectivity is determined by comparing the shock reflectivity to that from the bare aluminum surface which has a known reflectivity of 0.85 ± 0.05 . The relative systematic error incurred in this process could be up to 10% of the measured signal while the relative statistical uncertainties in the reflectivity are also $\sim 10\%$. The measured reflectivity versus shock speed and pressure for a decaying shock wave is shown in Fig. 2.

Comparing our Hugoniot data with various theoretical models, as shown in Fig. 1, indicates that the SESAME database (Table No. 7411 for sapphire and No. 7270 for LiF) [20] provides a good description of the EOS of sapphire and LiF between 10 and 20 Mbar. For sapphire, the data are also consistent with both quotidian EOS (qEOS) models [21,22]; for LiF the data appear to favor

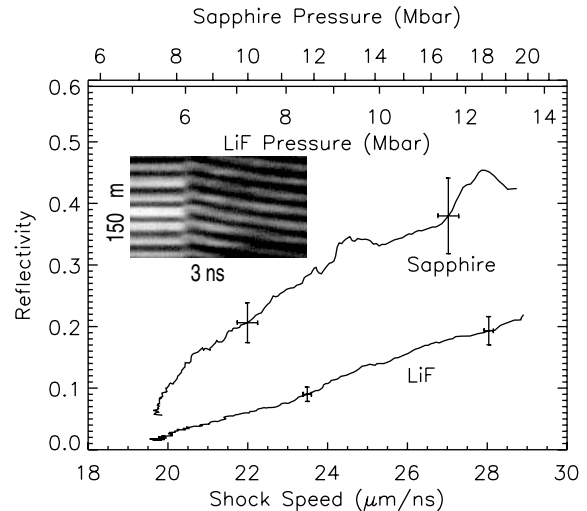


FIG. 2. Shock reflectivity as a function of shock speed in sapphire and LiF as determined from a decaying shock wave. Pressure values are calculated from the SESAME table. Error bars are shown for two typical points on each data set. The inset shows a portion of the VISAR image before and after shock breakout for the decaying shock in sapphire.

SESAME over qEOS, though, since the error bars represent 1σ uncertainties, qEOS is still consistent with the data. In the following discussion we will always use SESAME to convert from shock velocity (our experimental observable) to pressure, density, and temperature.

In the pressure range examined in our experiments, both sapphire and LiF are likely in the liquid phase. For LiF, previous experiments determined the melting pressure to be at 2.8 Mbar or less [13,14], well below the region probed in our studies. For sapphire, the melting pressure on the Hugoniot has never been measured; however, based on our Simon equation fits to previously published MD simulations [8] for the melting curve, we estimate that sapphire melts at 4–5.5 Mbar on the Hugoniot, below our lowest measured pressure. Indirect evidence for the existence of a phase transition in sapphire in this pressure range can be found by examining the Hugoniot data for sapphire shown in Fig. 1(a), where the linear U_s (shock velocity) to U_p (particle velocity) relation found in measurements below 3.4 Mbar [9] diverges significantly from our data when extrapolated to higher pressures. In contrast, good agreement is achieved for LiF when a similar extrapolation to high pressures is performed using data from below 4.8 Mbar [15]. Such a strong divergence is generally indicative of a phase transition in the intermediate region.

Shock front reflectivities much greater than a few percent are a clear indication that delocalized electrons are present in the shocked liquid [23]. Fresnel reflectivities (due to bound electron contributions) are estimated to be only $\sim 0.1\%$ based on extrapolations of the scaling found in previous experiments [6,12,13,24]. To understand the origin of such delocalized electrons we first note that for strong shocks, the thermal energy increases much more rapidly than the compressive energy. Over the gradual increase in reflectivity shown in Fig. 2 shock temperatures increase by a factor of 3, from 1.6 to ~ 5 eV, while compression ratios rise by a factor of only 1.25, from ~ 2 –2.5.

To quantitatively describe this behavior, we now construct a simple semiconductor model, with a band gap varying linearly in ion density, to predict the conduction electron density as a function of temperature, then use this in a Drude-type model to determine the dielectric constant and hence reflectivity of the shock front. The number density of conduction electrons in an intrinsic semiconductor is given by [25] $N_e = 2(mk_B T / 2\pi\hbar^2)^{3/2} \times F(-E_g/2k_B T)$ where m is the effective electron mass, k_B is Boltzmann's constant, T is the temperature, E_g is the energy gap in the electronic density of states (which is allowed to vary linearly with mass density), and $F(\eta) = 2/\sqrt{\pi} \int_0^\infty \sqrt{x}/[1 + \exp(x - \eta)]dx$ is a Fermi-type integral. In the limit $k_B T \ll E_g$, the conduction electron population is nondegenerate and $F(\eta)$ reduces to an exponential function with the result that $N_e \sim \exp(-E_g/2k_B T)$. Since shock temperatures in our experiments are several eV, of the same order as typical band gaps, electron populations

are partially degenerate and the full integral is required. We assume that the effective electron mass is equal to the free-electron mass, m_e . This appears reasonable for the liquid state and was found to give good results for the conductivity of a wide range of liquid metals [26]. Note that in this analysis we also assume that the free-electron states are singly degenerate.

With this electron density, $N_e(T)$, we can determine the relative dielectric constant from $\epsilon = \epsilon_b[1 - \omega_p^2/\omega^2(1 + i/\omega\tau)]$ where ϵ_b is the contribution due to bound electrons, $\omega = 3.5 \times 10^{15} \text{ s}^{-1}$ for 532 nm light, and τ is the electron relaxation time. The plasma frequency $\omega_p^2 = N_e e^2 / \epsilon_b \epsilon_0 m^*$, where N_e is the number of free electrons, e is the electron charge, ϵ_0 is the permittivity of free space, and m^* is the reduced mass of the electron, $m_e/2$, characteristic of a semiconductor resulting from the presence of holes. The relaxation time is taken as $\tau = \gamma\tau_{\min}$ where $\tau_{\min} = l/v_e$ is the minimum scattering time and $\gamma \geq 1$. For a material at the Ioffe-Regel limit, $\gamma \sim 1$. Here $l = 2(3/4\pi N_i)^{1/3}$ is the interatomic distance, where N_i is the total number of atoms per unit volume (Al and O or Li and F) and v_e is the average electron velocity computed by integrating over the Fermi distribution at a given temperature. The complex index of refraction, given by $n = \sqrt{\epsilon}$, can then be used to calculate the reflectivity from $R = |(n - n_{00})/(n + n_{00})|^2$, where $n_{00} = 1.39(1.77)$ is the index of unshocked LiF (sapphire). The value of $\epsilon_b = n_0^2$ is taken from the estimated shocked index of refraction n_0 based on extrapolation from previous work ($n_0 = 0.94n_{00}$ for sapphire [6,24] and $n_0 = 1.07n_{00}$ for LiF [12,13]). Expected uncertainties in these extrapolations have a minimal effect on the resulting reflectivity prediction [27].

Using this model we can calculate the semiconductor reflectivity at a known T and N_i subject to three unknown parameters: the energy gap constants A and B in $E_g(\rho) = A + B\rho$ and the relaxation time factor $\gamma = \tau/\tau_{\min}$. To determine these unknowns we perform a least-squares fit of the model to the measured shock reflectivity as a function of T and ρ . The results are illustrated in Fig. 3, where the reflectivity is plotted versus T , and show that the model reproduces the form of the reflectivity rise for both sapphire and LiF very well. At best fit, for sapphire, $\tau = 1.9\tau_{\min}$ while E_g drops slightly over the observed range from 2.7 to 1.6 eV; similarly for LiF, $\tau = 0.9\tau_{\min}$ at best fit and E_g rises slightly from 3.3 to 3.9 eV over the observed range. Errors in the inferred gap are ~ 2 eV, since at these high temperatures (unlike at room temperature) changes in the energy gap of the order of an eV do not significantly alter the conduction electron density. Thus the slight changes in gap energy over the observed range are not statistically significant. In contrast, small changes in τ produce significant changes in the steepness of the reflectivity rise since $\omega\tau \lesssim 1$, allowing τ to be determined to a precision of $\sim 20\%$ – 30% .

For insight into the conditions at the onset of significant electron delocalization we use this model to

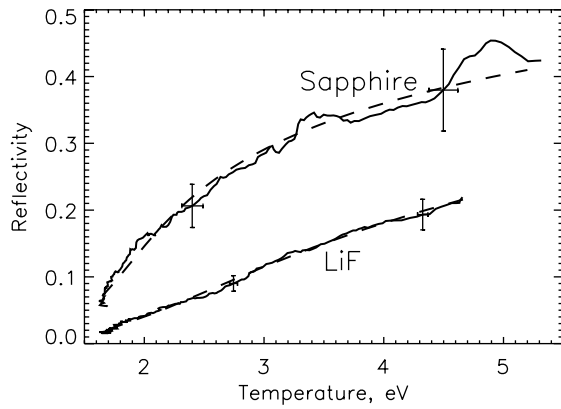


FIG. 3. Reflectivity data plotted versus T are shown with the best fit results (dotted lines) for τ and $E_g(\rho)$ from the semiconductor model. For sapphire, the average E_g over the observed range is ~ 2 eV while $\tau = 1.9\tau_{\min}$. For LiF, the average E_g is ~ 3.5 eV over the observed range, while $\tau = 0.9\tau_{\min}$.

calculate some important physical parameters. For sapphire at $\sim 5\%$ reflectivity (results are similar for LiF), the conduction electron density is $4 \times 10^{21} \text{ cm}^{-3}$ (compared to an atomic density of $2.2 \times 10^{23} \text{ cm}^{-3}$), the dc conductivity is $500 \Omega^{-1} \text{ cm}^{-1}$ and the electron DeBroglie wavelength (7 \AA) is close to the interatomic spacing (2 \AA), satisfying the conditions required for the Ioffe-Regel limit to be applicable [1]. The Fermi energy, E_F , of conduction electrons (1 eV) is similar to the temperature (1.7 eV) as expected for a semiconductor where $E_g \sim k_B T$. In contrast, for deuterium at saturated reflectivity [3], $E_F \gg k_B T$, indicating that the Fermi level is located in the conduction band as required for metallic behavior.

In developing this model, we have attempted primarily to provide a simple, physical picture to explain the gradual rise in reflectivity with shock strength observed in these initially wide band-gap insulators. By treating these materials as semiconductors pinned near the Ioffe-Regel limit we show quantitatively how the continuous reflectivity rise is a direct result of thermal activation of charge carriers across a reduced energy gap. A further feature of the model is that the reflectivity rise observes no discontinuity if the energy gap goes to zero or, in fact, becomes negative. It is straightforward to show that for a negative energy gap, the difference between the Fermi level and the bottom of the conduction band is just $-E_g/2$ and the model describes a free-electron metal. Thus at high temperatures, the phenomenon of gap closure is accompanied by no discontinuous feature and can be hidden in the gradual reflectivity rise, smoothing the semiconductor-to-metal transition.

We thank W. Unites, LLNL target fabrication, and the OMEGA operations staff for their efforts. This work was performed under the auspices of the U.S. D.O.E. by LLNL under Contract No. W-7405-ENG-48.

- [1] N. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1990).
- [2] S.T. Weir, A.C. Mitchell, and W.J. Nellis, Phys. Rev. Lett. **76**, 1860 (1996); W.J. Nellis, S.T. Weir, and A.C. Mitchell, Phys. Rev. B **59**, 3434 (1999).
- [3] P.M. Celliers *et al.*, Phys. Rev. Lett. **84**, 5564 (2000).
- [4] P.M. Bell, J.A. Xu, and H.K. Mao, *Shock Waves in Condensed Matter, 1985*, edited by Y.M. Gupta (Plenum, New York, 1986), p. 125.
- [5] L.M. Barker and R.E. Hollenbach, J. Appl. Phys. **41**, 4208 (1970).
- [6] S.C. Jones, B.A.M. Vaughan, and Y.M. Gupta, J. Appl. Phys. **90**, 4990 (2001).
- [7] G.Y. Shen and P. Lazor, J. Geophys. Res. **100**, 17699 (1995).
- [8] R. Ahuja, A.B. Belonoshko, and Borje Johansson, Phys. Rev. E **57**, 1673 (1998).
- [9] D. Erskine, in *High Pressure Science and Technology - 1993*, edited by S.P. Schmidt *et al.* (AIP, New York, 1994), p. 141.
- [10] T. Mashimo *et al.*, Geophys. Res. Lett. **27**, 2021 (2000).
- [11] N. Funamori and R. Jeanloz, Science **278**, 1109 (1997).
- [12] J.L. Wise and L.C. Chhabildas, *Shock Waves in Condensed Matter, 1985*, edited by Y.M. Gupta (Plenum, New York, 1986), p. 441.
- [13] S.B. Kormer, Sov. Phys. Usp. **11**, 229 (1968).
- [14] R. Boehler, M. Ross, and D.B. Boercker, Phys. Rev. Lett. **78**, 4589 (1997).
- [15] L.V. Al'tshuler *et al.*, Sov. Phys. Solid State **5**, 203 (1963); S.B. Kormer *et al.*, Sov. Phys. JETP **20**, 811 (1965).
- [16] T.R. Boehly *et al.*, Opt. Commun. **133**, 495 (1997).
- [17] L.M. Barker and R.E. Hollenbach, J. Appl. Phys. **43**, 4669 (1972).
- [18] P.M. Celliers *et al.*, Appl. Phys. Lett. **73**, 1320 (1998).
- [19] The velocity sensitivity for the two VISAR instruments was 9.006 and $3.988 \mu\text{m/ns/fringe}$ for sapphire and 11.45 and $5.069 \mu\text{m/ns/fringe}$ for LiF.
- [20] S.P. Lyon and J.D. Johnson, Los Alamos National Laboratory Report No. LA-UR-92-3407, 1992.
- [21] R.M. More *et al.*, Phys. Fluids **31**, 3059 (1988).
- [22] D.A. Young and E.M. Corey, J. Appl. Phys. **78**, 3748 (1995).
- [23] Reflectivity is that between shocked and unshocked state.
- [24] N.M. Balzaretti, J.P. Denis, and J.A.H. da Jornada, J. Appl. Phys. **73**, 1426 (1993).
- [25] See, for example, C. Kittel and H. Kroemer, *Thermal Physics* (W.H. Freeman and Co., San Francisco, 1980), 2nd ed., p. 366.
- [26] N.W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).
- [27] For sapphire, uncertainties in n_0 incurred by extrapolating previously reported measurements up to compressions of $2-2.5$ are $\sim \pm 5\%$. The resulting uncertainties in inferred τ and E_g are $\sim 7\%$, smaller than the fit uncertainties, and do not justify allowing n_0 to vary over the observed pressure range. For LiF, n_0 is known more accurately and extrapolation errors are only 1% .